Observation of a Narrow Pseudogap near the Fermi Level of AlCuFe Quasicrystalline Thin Films

T. Klein,[1,2] O. G. Symko,[1,*] D. N. Davydov,[3] and A. G. M. Jansen[3]

[1]*Department of Physics, University of Utah, Salt Lake City, Utah 84112*

[2]*Laboratorie d'Etudes des Propriétés Electroniques des Solides, Centre National de la Recherche Scientifique, BP 166, 38042 Grenoble Cedex 9, France*

[3]*High Magnetic Field Laboratory, Max Planck Institut für Festkorperforschung, Centre National de la Recherche Scientifique, BP 166, 38042 Grenoble Cedex 9, France*

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We present the first experimental determination by tunneling spectroscopy of the density of states (DOS) close to the Fermi energy of AlCuFe quasicrystalline thin film samples. The measurements show that the Fermi level in a quasicrystal lies in a deep narrow pseudogap 60 meV wide. Above an applied voltage of 50 mV a $V^{1/2}$ contribution to the DOS is observed in agreement with electron-electron interaction effects.

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Since the discovery of quasicrystalline samples (QC) with very high structural quality in the AlCuFe system [1] many papers have been devoted to the study of the unusual physical properties of this new phase of the condensed matter [2,3]. The very high resistivity values rising up to 10^7 $\mu\Omega$ cm at very low temperature in the new AlPdRe system [4] are among the most striking ones. There has been considerable interest in developing theoretical models for the conductivity in this system [5–7]. The thermopower [3] and the Hall effect [3,8] present very unusual temperature dependence which could only be described by assuming a very strong change in the conductivity [i.e., the density of states (DOS)] on an energy scale of about 100 meV [3,9]. The presence of a Hume-Rothery-like pseudogap, related to Brillouin scattering, has been predicted [10] and observed by x-ray emission [11] and photoemission spectroscopy [11,12], but those measurements led to a much wider pseudogap, of the order of 1 eV. However, linear muffin-tin orbital (LMTO) calculations of crystalline approximants [13,14] suggested the existence of very spiky substructures in the DOS with bandwidths as small as 10 meV. The presence of these structures may play a very important role in the physical properties of quasicrystals as well as in the stability of this new phase but no direct experimental evidence for their existence has been given so far.

The main result of this paper is the first high resolution measurement of the DOS close to the Fermi energy of quasicrystals performed by tunneling spectroscopy on AlCuFe thin films. We show that the variation of the DOS (ΔN) normalized to its value at the Fermi level (N_0) can be written as

$$\Delta N(E,T)/N_0 = \sqrt{E/\Delta(T)} + \delta N(E), \qquad (1)$$

where E is the energy, T is the temperature, $\sqrt{E/\Delta(T)}$ can be attributed to electron-electron interactions [15] characterized by a correlation gap $\Delta(T)$, and $\delta N(E)$ is the one-electron density of states which presents a very strong energy dependence, in agreement with the LMTO calculations [13,14].

The thin films, 3000 Å thick, have been fabricated by solid state interdiffusion of rf sputtered Al, Fe, and Cu layers on $SrTiO_3$ substrates. The thickness of each layer has been carefully adjusted in order to get the correct nominal composition. To ensure good thickness homogeneity the sample holder was set to oscillate back and forth at 0.5 Hz under the targets. The films were subsequently annealed in a quartz tube under high vacuum (10^{-6} Torr), first at 350 °C overnight and then at 600 °C for 2 h. The samples had resistivities between 2000 and 3000 $\mu\Omega$ cm at room temperature and they showed a strong negative temperature dependence of the resistivity, in agreement with observations on bulk materials of similar resisitivities. Besides such electrical characterization, x-ray diffraction patterns confirmed the quasicrystalline structure of the films. Details about the sample preparation procedure have been given elsewhere [16].

Tunneling spectroscopy measurements were performed using a scanning tunneling microscope with a platinum tip counter electrode. I-V curves were taken between 77 and 1.7 K and the tunneling resistances were between 20 kΩ (corresponding to the natural oxide barrier) and 10 MΩ (vacuum barrier). These curves were highly nonlinear, indicating that the tunneling conductance (G) was dependent strongly on the bias voltage. Although always present, this anomaly of the tunneling conductance could vary in amplitude from place to place by at most a factor of 2 and this can be attributed to small inhomogeneities in the film. No anomaly was observed in a pure aluminum film taken as a reference and we did not see any significant effect of the tunneling resistance on the data.

The voltage dependence of the tunneling conductivity (ΔG) is related to the variation of the DOS through the standard equation [17]

$$\Delta G/G = \int [\Delta N(E,T)/N_0] \frac{d}{dE}[-f(E + eV)]\,dE, \qquad (2)$$

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where f is the Fermi-Dirac distribution and $\Delta G/G = \Delta N(E)/N_0$ at $T = 0$. A typical tunneling spectrum of $\Delta G/G_0$ (normalized to zero bias) taken at 3.0 K is represented in Fig. 1(a), showing that the DOS of this quasicrystalline thin film is rapidly changing (by more than 100%) close to E_F. The pseudogap here is almost symmetric about E_F. The temperature dependence of the spectra between 1.7 and 4.2 K is presented in Fig. 1(b).

Figure 2 presents the energy dependence of the DOS on log-log scale. Two regimes can easily be identified: $\Delta N \sim E^2$ for $E < 50$ meV and a flattening out to a $E^{1/2}$ contribution above 50 meV. This $E^{1/2}$ contribution to the DOS can be attributed to Coulomb interactions, in agreement with the theory of Altshuler and Aronov for electron-electron interactions [15] and the theory of the metal-insulator transition developed by McMillan [18]. Quantum interference effects have been observed in both the temperature and magnetic field dependence of the conductivity [2,3]; electron-electron interaction effects appear to be dominant in the magnetoresistance of QC's at low temperature, suggesting that correlation effects may play an important role in the metal-insulator process in QC's. To obtain the one-electron DOS of the quasicrystalline structure $[\delta N(E)]$, we subtracted the $E^{1/2}$ behavior from the data. The result, which is almost temperature independent (except for the noise at high bias voltages), is presented in Fig. 3, at 4.2 K, for instance. This figure shows that the DOS of this quasicrystalline sample has a narrow pseudogap 60 meV wide close to E_F. As mentioned in the introduction, this pseudogap does not correspond to the wide (1 eV) Hume-Rothery-like pseudogap predicted by the models but rather to one of the spiky substructures predicted by LMTO calculations. The width of these structures can vary from about 100 to less than 10 meV, depending on the position of the Fermi energy, and thus it is reasonable to assume that our pseudogap corresponds to one of those structures. It is close to the activation gap of about 50 meV determined by Perrot and Dubois [19] in their interpretation of the temperature dependence of the thermal diffusivity of bulk quasicrystalline AlCuFe above room temperature.

Pierce *et al.* [9] first pointed out that the unusual temperature dependence of the thermopower could be

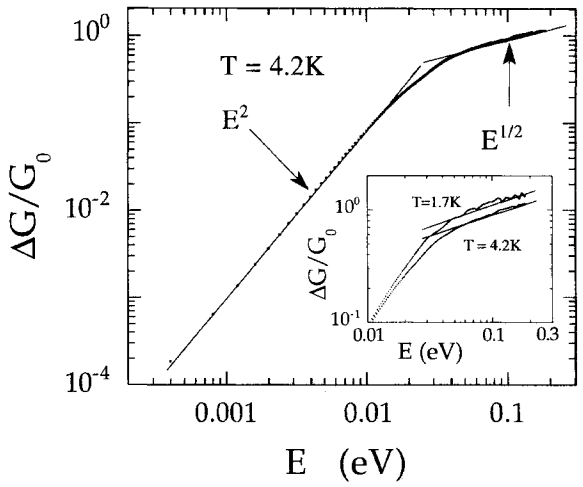

FIG. 2. Tunneling conductance change $\Delta G/G_0$ normalized to zero bias as a function of energy on a log-log plot showing two different regimes ($R_0 = 70$ kΩ). In the inset, temperature dependence of the slope of the $E^{1/2}$ regime is shown.

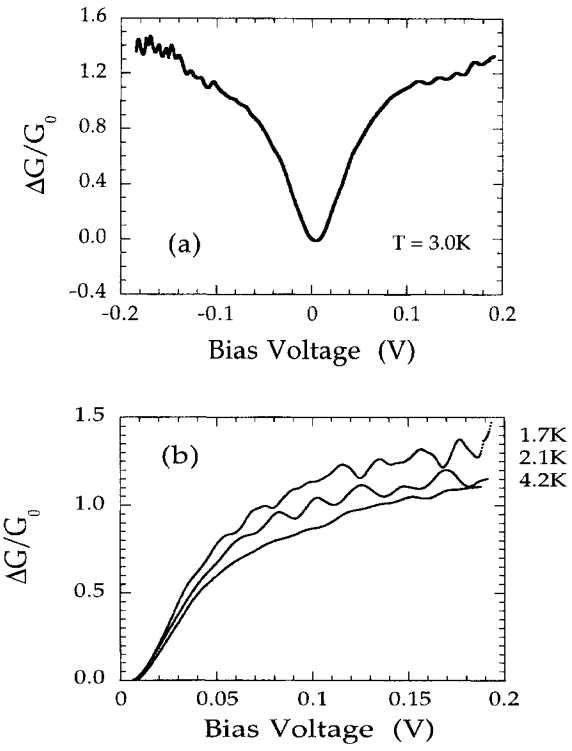

FIG. 1. (a) Tunneling conductance change $\Delta G/G_0$ normalized to zero bias as a function of applied voltage of AlCuFe quasicrystalline thin film at 3.0 K ($R_0 = 70$ kΩ). (b) Temperature dependence of the tunneling spectra between 1.7 and 4.2 K.

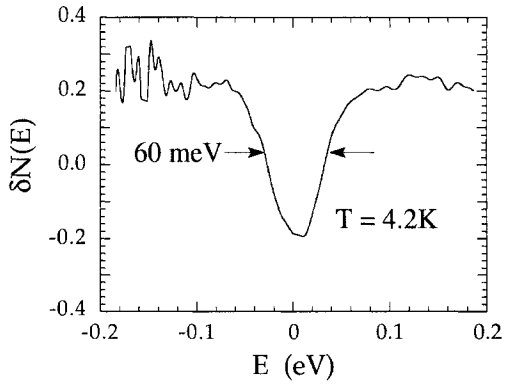

FIG. 3. One-electron density of states of the quasicrystalline structure (see text for details) showing a narrow pseudogap 60 meV wide.

explained by assuming that the conductivity is rapidly changing on an energy scale of about 100 meV; this is consistent with our determination of $N(E)$. Moreover, Matsuo *et al.* [20] have shown that the magnetic susceptibility of AlCuFe samples is proportional to T^2 above room temperature and this can be attributed to the energy dependence of the DOS (in the Pauli paramagnetism) assuming $d^2N(E_F)/dE^2 \sim 5 \times 10^6$ states/(Ry)^3 atom. Both specific heat [2,3] and NMR [21] measurements show a large reduction in the density of states of quasicrystals which is $N_0 \sim 0.14$ state/eV atom. Although there are strong variations of the conductivity with samples, N_0 is almost sample independent. Our experimental results show that $d^2N(E_F)/dE^2 \sim 10^6$ states/(Ry)^3 atom; this is close to the value expected from magnetic susceptibility measurements. A similar value of $d^2N(E_F)/dE^2 \sim 2 \times 10^6$ states/(Ry)^3 atom was used in the analysis of the uncommon temperature dependence of the spin-lattice relaxation in NMR experiments performed on high structural quality samples of another quasicrystal, AlCuRu [22]. Finally, we note that in the AlCuFe system the quasicrystalline structure can only be obtained in a very narrow composition range between $Al_{63}Cu_{25}Fe_{12}$ and $Al_{62.5}Cu_{25}Fe_{12.5}$; taking the electronic valence to be +3, +1, and −2.4 [23] for Al, Cu, and Fe, respectively, the change in the average number of electrons per atom corresponds to a shift in energy of 150 meV, which is close to the bandwidth at the top of our pseudogap. This pseudogap may thus play an important role in the stabilization process of the quasicrystalline structure as pointed out by Phillips [24] from geometric and chemical arguments.

We also measured tunneling spectra at 77 K. At this temperature the electron-electron interactions contribution can be neglected and, even if the change in conductance may not be related exactly to the change in the DOS [according to Eq. (2)], such measurement will provide information on $\delta N(E)$. As shown in Fig. 4, $\Delta G/G_0$ presents at this temperature a strong voltage dependence and the pseudogap, obtained after subtraction of the usual quadratic background of the junction, is now experimentally more smeared out by a few kT to about 100 meV in width (at low temperature this background represents only about 5% of the signal in our range of voltage bias and hence we neglected it).

As to the $E^{1/2}$ dependence of the DOS, expected for electron-electron interactions effects, its slope of $1/\Delta^{1/2}$ is slightly temperature dependent indicating that the Coulomb gap is getting wider as its amplitude decreases with temperature (Fig. 2, inset). The value of Δ is about 0.13 eV at 1.7 K, in good agreement with values measured in metal-insulator systems of comparable resistivities [25] (about 4500 $\mu\Omega$ cm at 1.7 K in this sample). The expression for $\Delta N/N_0$ due to electron-electron interactions has been given by Altshuler and Aronov [15] as

$$\Delta N/N_0 = [\lambda/2.82dN_0\pi^2(hD)^{3/2}]E^{1/2}, \qquad (3)$$

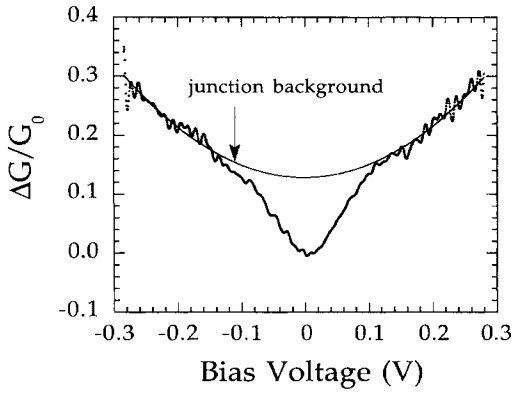

FIG. 4. Tunneling spectrum of an AlCuFe quasicrystalline thin film at 77 K.

with $\lambda = 4 - 3(1 + F/2)^{1/2}$, where F is the Coulomb screening factor estimated to be about 0.63 in bulk $Al_{63}Cu_{25}Fe_{12}$ quasicrystalline samples [2], D is the diffusion coefficient, d is the atomic concentration ($d = 6 \times 10^{22}$ atoms/cm^3), and $N_0 = 0.14$ state/eV atom. Finally, by estimating D from the Einstein equation $\sigma = e^2N_0D$, we get for our case $\Delta N/N_0 = 2.4V^{1/2}$ (where V is the bias in volts) which is in good agreement with our experimental results ($2.1V^{1/2}$ at 4.2 K and $2.7V^{1/2}$ at 1.7 K). Our measurements confirm the idea of localization effects in the presence of strong electron-electron interaction effects as found from the magnetic field dependence of the conductivity [2]. An $(E - E_F)^{1/2}$ anomaly in the DOS has also been predicted by Janot and DeBoissiew [7] from a hierarchical construction of the quasicrystalline structure. Although an asymmetric and temperature independent contribution was expected, our data seem to rule that out. However, that theory is expected to be applicable only for energies much smaller than $\hbar/\tau_e$, where τ_e is the elastic scattering time. Assuming τ_e to be of the order 10^{-14} s (following [6]) we would have expected to observe this dependence only for voltages much smaller than 100 mV.

In conclusion, we have presented the first high resolution experimental determination of the density of states close to the Fermi level in an AlCuFe quasicrystalline thin film. The measurements show that the DOS in the quasicrystalline structure presents a strong energy dependence at E_F, indicating that the Fermi level is lying close to the bottom of a narrow pseudogap (60 meV wide); this is in agreement with recent LMTO calculations and it has fundamental consequences for our understanding of quasicrystals. For higher bias voltages $\Delta N/N_0$ is proportional to $V^{1/2}$ as predicted by electron-electron interaction theories. The presence of this correction to the one-electron DOS indicates that Coulomb interactions may play an important role in the metal-insulator mechanism observed in quasicrystals.

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*To whom correspondence should be addressed.

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